

Heterogeneous Nucleation in the Low Barrier Regime

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(Dated: August 7, 2012)

In simulations of the 2D Ising model, we examine heterogeneous nucleation induced by a small impurity consisting of a line of l fixed spins. As l increases, we identify a limit of stability beyond which the metastable phase is not defined. Approaching the limit of stability, we evaluate $G(n)$, the free energy when the system contains an n -site cluster of the stable phase attached to the impurity. We show that the conventional definition of the nucleation barrier as the difference between the minimum and the maximum (at $n = n^*$) of $G(n)$ gives poor results when used to predict the nucleation time (from classical nucleation theory) and the size of the critical cluster (from the nucleation theorem). However, if the barrier is defined relative to a reference state that considers the entire configuration space of the metastable phase (i.e. all $n < n^*$), then the predictions of theory are excellent. Under the latter definition we show that, contrary to expectations, the nucleation barrier does not vanish at the limit of stability.

Classical nucleation theory [1–3] (CNT) continues to be of fundamental importance for understanding phase transformations in a great variety of systems. The assumptions upon which CNT is based nominally restrict the theory's ability to predict nucleation rates to systems that are only mildly metastable and for which the nucleation barrier is large relative to kT , where T is the temperature and k is Boltzmann's constant. However, many interesting phase changes occur in the deeply metastable regime where the system is approaching a limit of stability and the free energy barrier to nucleation is expected to disappear [4, 5]. Some recent simulation studies [6–8] find that the general features of CNT remain surprisingly robust in this deeply metastable regime, but others suggest that CNT breaks down [4, 9, 10]. Understanding whether CNT remains applicable, or how the theory must be adapted, when the nucleation barrier becomes low remains an open question.

The presence of a heterogeneous interface in a metastable system can dramatically lower the nucleation barrier in phase transformations such as vapor condensation and crystallization [11, 12]. Consequently, heterogeneous nucleation plays an important role in a variety of phenomena including atmospheric physics [13, 14], the use of templates to form complex structures [15–17] and protein crystallization [18]. The basic principles of heterogeneous nucleation involving macroscopic, bulk surfaces are relatively well established. However, in many cases the heterogeneities are microscopic in size and there is considerable interest in understanding how particle size influences the nucleation mechanism and rate [14, 16, 17, 19–22], especially as the barrier approaches kT .

In this Letter, we study heterogeneous nucleation in the two-dimensional (2D) Ising model to explore the nature of the nucleation barrier on approach to the limit of

stability of a metastable phase. We seek to clarify the definition of the barrier in this limit, and to test the degree to which theories (in particular CNT, and also the nucleation theorem) are able to predict the behaviour observed directly in this regime. The Ising system we examine was studied previously by Sear [20], who demonstrated that a small cluster of fixed “impurity” spins increased the nucleation rate significantly relative to the homogeneous nucleation rate. In the present study, we exploit the fact that by increasing the size of the impurity we can systematically lower the nucleation barrier and also bring the system to a limit of stability. At the same time, this simple model permits a rigorous evaluation of the free energy barrier, critical cluster size, and nucleation rate, facilitating the comparison of theory with direct observations.

Our results are based on Monte Carlo (MC) simulations of a 2D Ising model of a ferromagnet on a $L \times L$ square lattice with $L = 45$, the same system size studied in Ref. [20]. The energy of the system in spin configuration c is given by,

$$E_c = -J \sum_{\langle i,j \rangle} s_i s_j + H \sum_{i=1}^N s_i \quad (1)$$

where $s_i = \pm 1$ is the spin value of site i , $J > 0$ quantifies the ferromagnetic exchange interaction, H is the value of the external magnetic field, and $N = L^2$ is the number of sites in the lattice. The sum in the first term is taken over all nearest-neighbor pairs of spins. We explore the configuration space of the system using a standard MC dynamics, in which one Monte Carlo step (MCS) corresponds to N spin-flip attempts, where spins are chosen at random.

To induce heterogeneous nucleation, our system contains an impurity consisting of a line of l spins fixed

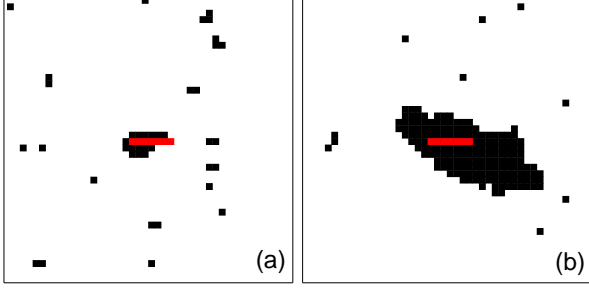


FIG. 1: Example configurations of the system in the metastable phase with $\beta J = 0.65$, $\beta H = +0.05$, and $l = 7$ (a) when $n = n_0 = 21$, and (b) when $n = n^* = 174$. Impurity sites are shown in red. Up-spins ($s_i = +1$) are shown in black, down-spins ($s_i = -1$) in white.

to $s_i = +1$. In each of our runs, we initialize all non-impurity spins to $s_i = -1$, and equilibrate the system in the spin-down phase at $\beta J = 0.65$ (i.e. 0.678 of the critical temperature) and $\beta H = -0.05$, where $\beta = 1/kT$. We then create a metastable state by instantaneously changing the sign of the magnetic field, so that $\beta H = +0.05$. Under these conditions the spin-down phase is metastable (see Fig. 1), and the system persists in this phase until nucleation of the stable spin-up phase occurs.

In the absence of an impurity, the transformation from the metastable to the stable phase occurs via homogeneous nucleation, for which the free energy barrier is $27kT$ [23, 24] and the system nucleation time is 1.5×10^9 MCS [25]. In the presence of the impurity, the phase transition occurs via heterogeneous nucleation. As we will show below, for $l \geq 3$, the height of the heterogeneous nucleation barrier is less than $14kT$, and the heterogeneous nucleation rate is more than 350 times faster than homogeneous nucleation. Homogeneous nucleation events (i.e. events that do not involve the impurity) are thus rare and can be neglected in our analysis.

To find the free energy barrier for heterogeneous nucleation, we seek to evaluate the minimum reversible work of formation of a critical cluster of the stable phase. Since homogeneous nucleation can be neglected, the critical cluster is necessarily a cluster of up-spins (i.e. sites with $s_i = +1$) attached to the impurity. In the following, we define the “impurity cluster” as the contiguous cluster of up-spins that contains the impurity spins; thus the number of spins n in the impurity cluster includes the impurity spins themselves. Under this definition there can only be one impurity cluster, and so n is a *system* property (and hence an order parameter) with respect to which the nucleation free energy barrier may be defined.

To define the system free energy for fixed (N, H, T, l) , we first write the partition function of the system $\mathcal{Z} = \sum_{n=l}^N Z(n)$ as a sum over the conditional partition function $Z(n) = \sum_{c(n)} \exp(-\beta E_c)$. The sum in $Z(n)$ is over

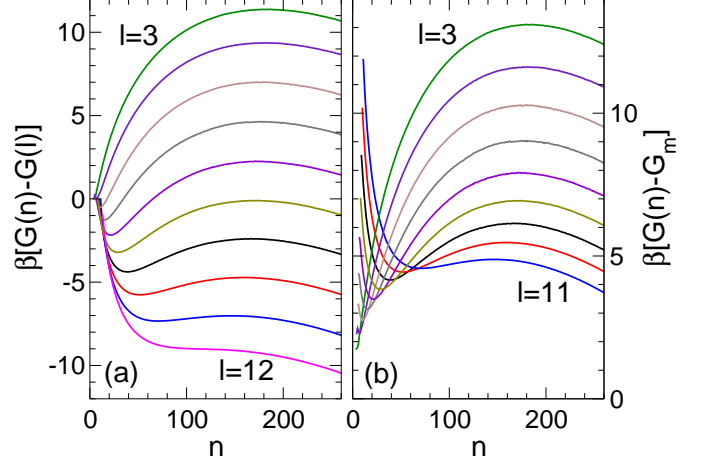


FIG. 2: (a) $G(n) - G(l)$ as a function of n for $l = 3$ to 12. (b) $G(n) - G_m$ versus n for $l = 3$ to 11. For all curves, the statistical error is less than $0.02kT$.

all system configurations c in which the impurity cluster consists of exactly n spins. The corresponding conditional free energy is $G(n) = -kT \log Z(n)$, which is the free energy of the system when it contains an impurity cluster of size n .

To compute $G(n)$, we note that the probability to observe an impurity cluster of n spins is $P(n) = Z(n)/\mathcal{Z}$. Consequently, the work of formation of an n -spin impurity cluster, starting from a “bare” impurity (i.e. $n = l$), is given by the free energy difference,

$$G(n) - G(l) = -kT \log \frac{Z(n)}{Z(l)} = -kT \log \frac{P(n)}{P(l)}. \quad (2)$$

To determine $G(n)$ in the region of the nucleation barrier, we impose a constraint on our MC sampling such that $n \leq n_{\max} = 300$. This choice of n_{\max} restricts our simulations to the metastable phase, and to configurations in the vicinity of transition states to the stable phase, without allowing the system to explore the stable phase itself.

We evaluate the equilibrium ratio $P(n)/P(l)$ from our simulations, and plot the result for $G(n) - G(l)$ in Fig. 2(a), for various l . For $3 \leq l \leq 11$, each curve exhibits a maximum at $n = n^*$, indicating the size of the critical cluster, and demarcating the boundary between the configuration space of the metastable phase (defined by $l \leq n \leq n^*$) and the stable phase ($n > n^*$). Also, as l increases, a minimum at $n = n_0$ emerges and grows; this feature corresponds to wetting of the impurity by a finite cluster of the stable phase. The variation of n^* and n_0 with l is shown in Fig. 3. Note that in Fig. 2(a), for $l = 12$, the variation of $G(n) - G(l)$ is monotonic in n , demonstrating that the limit of stability of the metastable phase has been exceeded. This limit of stability is also seen in Fig. 3 as n^* and n_0 approach one

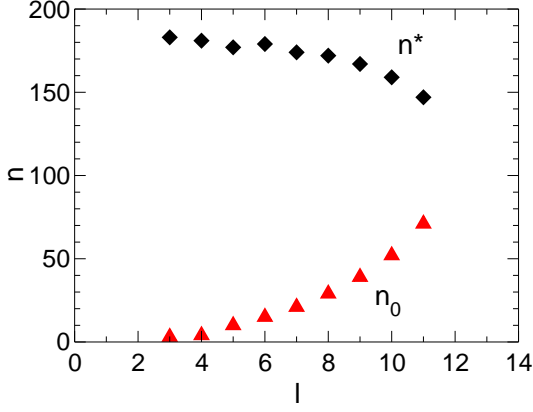


FIG. 3: n^* and n_0 as a function of l . Statistical errors are smaller than the symbol size.

another, and then cease to be defined for $l \geq 12$.

To obtain the free energy barrier for nucleation from $G(n)$, we must identify an appropriate reference state with respect to which the barrier height will be measured. When both a minimum and a maximum appear in a free energy profile, previous works (see e.g. Refs. [5, 12, 17]) have defined the free energy barrier for nucleation as $\Delta G_0 = G(n^*) - G(n_0)$, i.e. the difference in $G(n)$ from the minimum at $n = n_0$ to the maximum at $n = n^*$. Our results for ΔG_0 as a function of l are shown in Fig. 4(a). Under this definition, the nucleation barrier goes to zero at the same l that corresponds to the loss of stability of the metastable phase.

However, the free energy barrier for nucleation is more accurately defined as the minimum reversible work required to apply a constraint that confines the system to the transition state at $n = n^*$, starting from a reference state that considers the entire configuration space of the metastable phase, i.e. all configurations in the range $l \leq n \leq n^*$. To implement this definition in the present system, we define the partition function of the metastable phase $Z_m = \sum_{n=l}^{n^*} Z(n)$ as a restricted sum over all states such that $l \leq n \leq n^*$. The corresponding free energy of the metastable phase is $G_m = -kT \log Z_m$. The work of formation of an n -spin impurity cluster, starting from the equilibrium metastable phase, is then given by the free energy difference,

$$\begin{aligned} G(n) - G_m &= -kT \log \frac{Z(n)}{Z_m} \\ &= -kT \log \frac{P(n)}{\sum_{n'=l}^{n^*} P(n')}. \end{aligned} \quad (3)$$

The second equality above emphasizes that $G(n) - G_m$ can also be evaluated in our simulations from the relative probabilities for observing the impurity cluster to have various n .

Our results for $G(n) - G_m$ are plotted in Fig. 2(b). The difference between the free energy curves in Fig. 2(a)

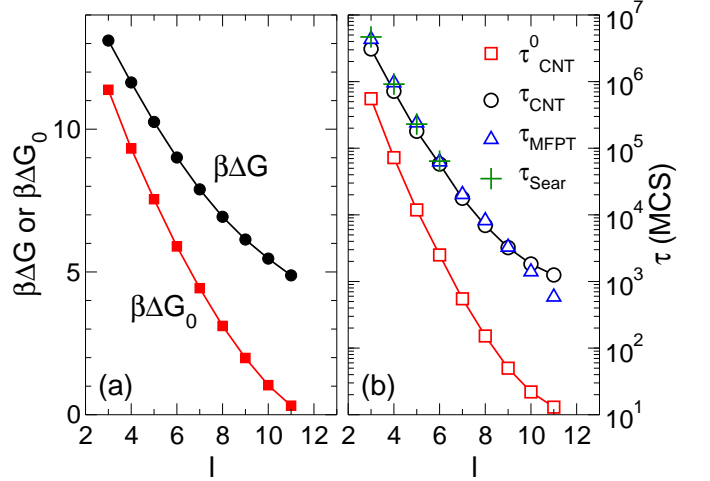


FIG. 4: (a) Comparison of ΔG and ΔG_0 as a function of l . (b) τ_{CNT}^0 , τ_{CNT} , τ_{MFPT} , and τ_{Sear} as a function of l . For comparison, note that the homogeneous nucleation time when no impurity is present is 1.5×10^9 MCS [20]. For all quantities, statistical errors are smaller than the symbol size.

and (b) is just a change in the reference state, and so the shapes of the curves do not change. However, the height of the nucleation barrier does change. Using the more accurate definition, the work of formation of the transition state from the metastable phase is given by $\Delta G = G(n^*) - G_m$. As shown in Fig. 4(a), ΔG does not go to zero at the limit of stability. Although paradoxical at first glance, this result is physically reasonable for our system. Since n^* remains non-zero even at the limit of stability, the metastable phase encompasses a considerable region of configuration space ($l \leq n \leq n^*$) up to the point where stability is lost. Hence the work required to create the transition state remains finite, even as the metastable state ceases to exist as a distinct phase. In previous work, it has been assumed that the nucleation barrier should go to zero as the thermodynamic stability of a metastable phase is lost [4, 5]. Our system provides a counter-example.

We next assess the implications of our results when estimating the nucleation time using CNT [24]. For our system, the CNT prediction for the nucleation time is,

$$\tau_{\text{CNT}} = (f_c^+ z)^{-1} \exp(\beta \Delta G), \quad (4)$$

where τ_{CNT} is the average time (in MCS) per impurity for a critical cluster to appear in the system that subsequently evolves into the stable phase. $z = \sqrt{\beta \eta / 2\pi}$ is the Zeldovich factor, where $\eta = -(\partial^2 G / \partial n^2)_{n=n^*}$ is the curvature of $G(n)$ at the top of the barrier. We estimate η from a quadratic fit to data that lies within $0.2kT$ of the maximum of $G(n)$. f_c^+ is the attachment rate of monomers to the critical cluster. We determine f_c^+ from the time dependence of fluctuations of the size of critical clusters, following the same procedure used in Ref. [24].

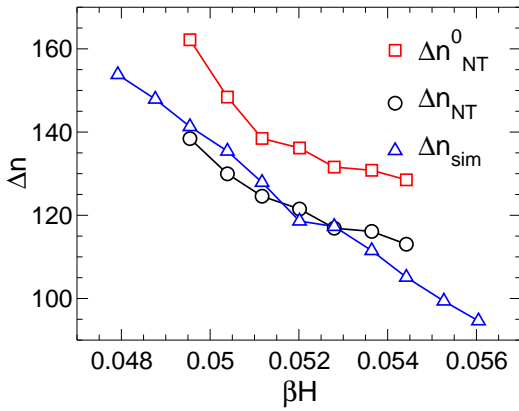


FIG. 5: Comparison of Δn_{NT} , Δn_{NT}^0 , and Δn_{sim} as a function of βH , for the $l = 7$ system.

The result for τ_{CNT} obtained from our data is shown in Fig. 4(b); we also show τ_{CNT}^0 , the CNT prediction for the nucleation time obtained if we use ΔG_0 instead of ΔG in Eq. 4. We find that for the lowest barriers (at large l), τ_{CNT} and τ_{CNT}^0 differ by more than two orders of magnitude, emphasizing the importance of selecting the correct definition of the free energy barrier in this regime.

To test the accuracy of τ_{CNT} , we directly evaluate the nucleation time in terms of the mean first passage time (MFPT) for the impurity cluster to grow to the critical size. For a given l , we set $n_{\text{max}} = n^*$ so that the system is confined to explore only the configuration space of the metastable phase, and bring this constrained system into equilibrium. Then, at a randomly selected time, we set $t = 0$ and measure the time it takes for the system to first reach $n = n_{\text{max}}$. The MFPT is the average of many such measurements. We define the nucleation time τ_{MFPT} as twice the MFPT, because only half of the runs that reach the transition state would ultimately evolve into the stable phase. As shown in Fig. 4(b), τ_{MFPT} is in excellent agreement with τ_{CNT} , but is clearly distinct from τ_{CNT}^0 . Fig. 4(b) also shows that τ_{MFPT} is consistent with the nucleation times (τ_{sear}) reported in Ref. [20] for the same system, as found using a forward-flux sampling method. Our observations not only validate the choice of ΔG over ΔG_0 for the nucleation barrier, but also demonstrate that in our case CNT is capable of predicting the nucleation time with remarkable accuracy even at the very limit of stability of the metastable phase.

Finally, it is also possible to test the validity of ΔG versus ΔG_0 as a measure of the nucleation barrier by exploiting the nucleation theorem. The nucleation theorem [26–30] states that,

$$\left(\frac{\partial \Delta G}{\partial \Delta \mu} \right)_T = \frac{1}{2} \left(\frac{\partial \Delta G}{\partial H} \right)_T = -\Delta n, \quad (5)$$

where $\Delta \mu$ is the difference in chemical potential between the stable and metastable phases, and Δn is the excess

number of up-spins in the critical cluster. In the first equality, we have used $\Delta \mu \approx 2H$, which for the Ising model is a good approximation for T below the Curie temperature [24, 31]. To conduct this test, we carry out new runs for the case of $l = 7$ over a range of βH from 0.048 to 0.056. We directly evaluate Δn as the difference in the average number of up-spins in the entire system (including those not in the impurity cluster) when the system is at $n = n^*$, and the average number of up-spins in the metastable phase averaged over all $l \leq n \leq n^*$; these results are shown in Fig. 5 and denoted as Δn_{sim} . We also evaluate ΔG and ΔG_0 as a function of H , and estimate the derivative in Eq. 5 using a five-point central difference numerical method. We thus obtain two estimates of Δn from the left-hand side of Eq. 5: Δn_{NT} is found using ΔG , while Δn_{NT}^0 is found using ΔG_0 . As shown in Fig. 5, Δn_{NT} is in distinctly better agreement with Δn_{sim} than Δn_{NT}^0 , providing additional confirmation that ΔG is the correct measure of the nucleation barrier.

We note that although the definitions of $G(n)$ and the nucleation barrier are straightforward in the present system, it remains a challenge to define the free energy of cluster formation in simulations of homogeneous nucleation when the barrier is low. In particular, in the homogeneous case, the cluster size n can only be used as an order parameter in the limit that the spontaneous formation of clusters is rare [32, 33], i.e. in the limit that there is at most one cluster in the system. However, $Z(n)$ [and hence $G(n)$] is not defined if n does not have a unique value for each system configuration, a complication that arises when the barrier is low because multiple clusters may form simultaneously. This difficulty is avoided here because homogeneous nucleation is negligible, and because a single impurity cluster is always well defined, regardless of the barrier height.

We also emphasize that the difference between ΔG and ΔG_0 is only apparent in the low barrier regime. When the barrier is high, even small clusters are rare, and the properties of the metastable phase are dominated by system configurations found near $n = l$. In this limit $G(l) \approx G_m$, and ΔG and ΔG_0 become equivalent. However, as we have seen, in the low barrier regime the distinction between ΔG_0 and ΔG becomes important. Our analysis shows that the selection of the correct thermodynamic reference state is crucial for identifying the nucleation barrier (ΔG) that is appropriate for studying low barrier systems. Using ΔG , we demonstrate that both CNT and the nucleation theorem are impressively accurate, even at the limit of stability. At the same time, we find that ΔG does not vanish at the limit of stability of the metastable phase. We expect that the pattern of behavior found here will be common to all low-barrier systems where a free energy minimum and maximum converge at a finite value of the order parameter, and thus may be generic for heterogeneous nucleation on small im-

purities. Only in the case that the size of the critical cluster goes to zero ($n^* \rightarrow 0$) should we expect that the nucleation barrier will vanish at the limit of stability.

We thank ACEnet and WestGrid for providing computational resources, and NSERC for financial support. PHP thanks the CRC program for support.

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